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(54) Photochromatic and thermochromatic compounds and their application in polymeric materials.

(57) A description follows of photochromatic and thermochromatic compounds, belonging to the group of spiro-indoline-oxazines, and their application in polymeric materials.

EP 0 524 692 A1

The present invention relates to photochromatic and thermochromatic compounds, belonging to the group of spiro-indoline-oxazines, and their application in polymeric materials.

Photochromatic compounds are substances which have the characteristic of reversibly changing colour and/or degree of light transmission when exposed to certain types of electromagnetic radiations and solar light, returning to their original state of colour and transmission when the initial light source is removed.

There are many known substances having photochromatic characteristics, belonging to different groups of both inorganic and organic compounds, as can be seen, for example, in the texts "Photochromism", by G.H. Brown (Ed.), Vol. III of the Weissberger series "Techniques of Organic Chemistry", Wiley Interscience, New York (1971) and in "Photochromism. Molecules and Systems", by H. Dürr and H. Bouas-Laurent (Ed.), Vol. 40 of the series "Studies in Organic Chemistry", Elsevier (1990).

Among the organic photochromatic compounds, particularly well-known are those of the group of spiro-indoline-oxazines which are capable of giving photochromatic characteristics to polymerized organic materials, used as photochromatic articles, as described for example in U.S. Patents 3.562.172, 3.578.602, 4.215.010, 4.342.668, EP 146.135, WO 85/02619, EP 245.020, EP 134.633, EP 141.407 and in Italian Patent Applications IT 22529 A/87, IT 22660 A/89 and IT 19389 A/90 in the name of the Applicant.

Known photochromatic compounds of the spiro-indoline-oxazine group, compared to other known organic photochromatic compounds (for example those belonging to the group of spiro-pyranes), have the advantage of having a much higher fatigue resistance when submitted to repeated coloration and de-coloration cycles and a much greater aging resistance on exposure to solar light or in artificial aging tests.

This behaviour is extremely advantageous for the above-mentioned uses.

The photochromatic compounds belonging to the group of spiro-indoline-oxazines of the known art cannot be used however in some polymeric materials such as high-density polyethylene, low-density polyethylene, ethylene-vinylacetate copolymer, polyether amides such as, for example PEBAX (Atochem).

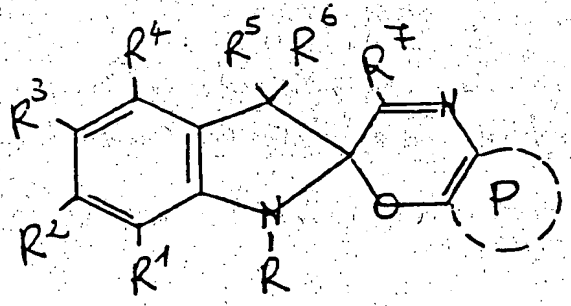
In these matrices, in fact, the photochromatic compound tends to appear on the surface of the product causing a phenomenon known as "blooming".

This draw-back prevents the above compounds from being applied in various fields such as agricultural covering sheets, bags, packaging and generally in areas where the above polymers are used.

We have now synthesized, and this forms the first aspect of the present invention, photochromatic and thermochromatic compounds, belonging to the spiro-indoline-oxazine group, having substituents composed of long alkyl chains, which overcome the above disadvantages of the known art.

A second aspect of the present invention relates to the photochromatic polymeric compositions obtained by superficially applying or incorporating the above compounds into suitable polymers.

The compounds of the present invention can be defined with the following general formula (I):



(I)

wherein:

1) R represents a hydrogen atom; a C_1-C_5 alkyl group linear or branched; a C_1-C_5 alkyl group substituted with from 1 to 5 halogen atoms selected from fluorine, chlorine, bromine and iodine, hydroxy groups, C_1-C_5 alkyoxy groups, C_1-C_5 alkyl carboxy groups, cyano groups; a C_2-C_5 alkenyl group; a phenyl group; a benzyl group;

2) R^1 to R^4, the same or different, each independently represent a hydrogen atom; a linear or branched C_1-C_5 alkyl group; a C_1-C_5 alkyl group substituted with from 1 to 5 halogen atoms selected from fluorine, chlorine, bromine and iodine, hydroxy groups, C_1-C_5 alkoxy groups, C_1-C_5 alkyl carboxy groups, cyano groups; a C_2-C_5 alkenyl group; a benzyl group; a halogen atom selected from fluorine, chlorine, bromine and iodine; a hydroxy group; a C_1-C_5 alkoxy group; an amino group; a mono-alkyl (C_1-C_5) amino group; a di-alkyl (C_1-C_5) amino group; a cyclo-alkyl (C_3-C_{10}) amino group; a piperidino, piperazino or mor-

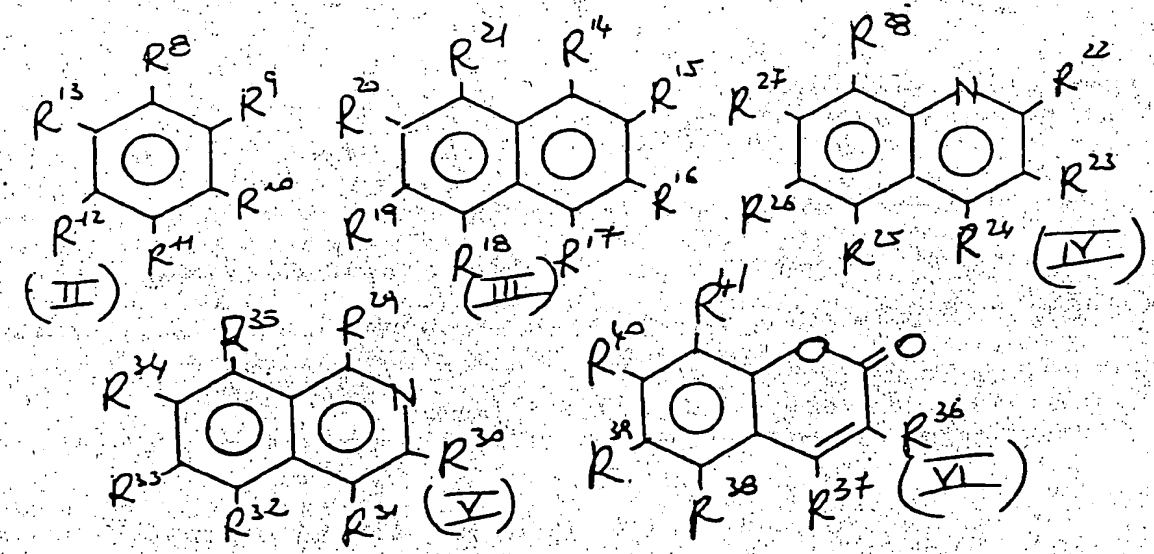
pholino group; a carboxyl group; a C_1-C_5 alkyl carboxy group; a C_2-C_5 alkenyl carboxy group; an amidic carboxy group; a substituted N-alkyl (C_1-C_5) amidic carboxy group; a substituted N,N-dialkyl (C_1-C_5) amidic carboxy group; a cyano group; a nitro group; a sulphonic group; a sulphonic alkyl (C_1-C_5) group; a trifluoromethan-sulphonic group; a sulphonic aryl group selected from sulphonic benzene groups, sulphonic p-toluene groups, sulphonic p-chlorotoluene groups; an aryl group selected from phenyl, biphenyl, naphthyl groups; an acylic group of the ketone alkyl, ketone aryl or ketone benzyl type;

3) two consecutive substituents from R^1 to R^4 can represent the fusion sites with other aromatic, heterocyclic or quinonic rings;

4) R^5 and R^6, the same or different, each independently represent a linear or branched C_1-C_5 alkyl group; a phenyl group; or R^5 and R^6, together with the carbon atom to which they are linked, jointly represent a C_4-C_7 cycloalkyl group;

5) R^7 represents a hydrogen atom; a linear or branched C_1-C_5 alkyl group; a phenyl group; a halogen atom selected from fluorine, chlorine and bromine; a C_1-C_5 alkoxy group, a phenoxy group;

6) P represents a monocyclic or polycyclic arenic nucleus, of the benzene, naphthalene, quinoline, isoquinoline or cumarin type which can be respectively represented by formulae (II), (III), (IV), (V) and (VI):



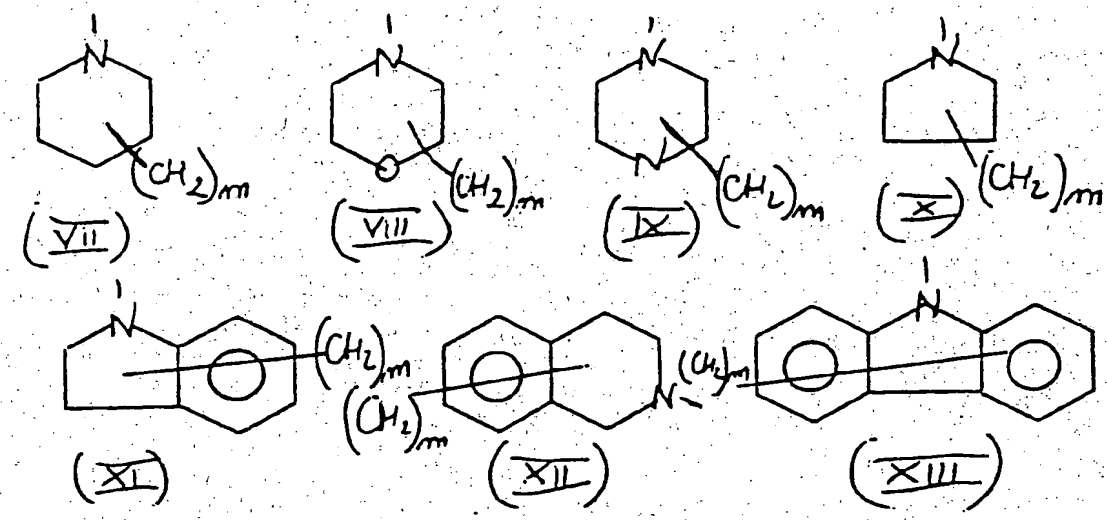
wherein:

6a) at least two contiguous substituents from R^8 to R^{13}, R^{14} to R^{21}, R^{22} to R^{28}, R^{30} to R^{35}, R^{35} to R^{41} represent the fusion sites with the oxazinic ring;

6b) the substituents from R^8 to R^{41} have the meaning defined in point 2);

7) at least one of the substituents selected from R-R^{41} represents an R^{42} group, a -$COOR^{42}$, -$CONHR^{42}$, -$CONR^{42}R^{43}$, -COR^{42}, OH-CH-R^{42}, OH-C-$R^{42}R^{43}$, -OR^{42}, -NHR^{42}, -$NR^{42}R^{43}$, -SR^{42}, -O-$(CH_2)_n$-$COOR^{42}$, -O-$(CH_2)_n$-$CONHR^{42}$, -O-(CH_2)-$CONR^{42}R^{43}$ group, wherein n varies from 0 to 10 and R^{42} and R^{43} can independently be a linear or branched C_6-C_{30} alkyl group; a C_6-C_{30} alkyl group substituted with 1-30 halogen atoms selected from fluorine, chlorine, bromine or iodine; a C_6-C_{30} alkenyl group.

Substituents R^1-R^{41} may otherwise be groups represented by formulae (VII)-(XIII):



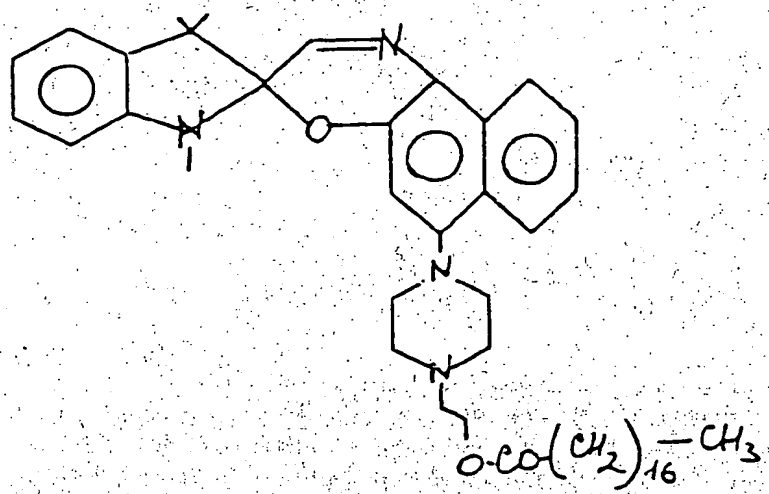
wherein m is an integer from 0 to 10.

In the preferred method, in formula (I):

- R represents a methyl, ethyl, benzyl, 2-allyl, 2-hydroxyethyl, 2-methoxyethyl or 2-carboxymethylethyl group;
- R^1 to R^4, the same or different, each independently represent the hydrogen atom, a fluorine, chlorine or bromine atom, a methyl, isopropyl, trifluoromethyl, hydroxymethyl, benzyl, hydroxy, methoxy, amino, piperidino, morpholino, carboxyl, carboxymethyl, N,N-dimethylcarboxyamide, cyano, nitro or phenyl group;
- R^5 and R^6, the same or different, each independently represent a methyl or phenyl group or, together with the carbon atom to which they are linked, jointly represent a cyclohexyl group;
- R^7 represents the hydrogen atom, chlorine atom or phenyl, methyl or methoxy group;
- P is one of the groups with a formula from (II) to (VI) wherein:
- two contiguous substituents from R^8 to R^{13}, R^{14} to R^{21}, R^{22} to R^{28}, R^{30} to R^{35}, R^{36} to R^{41} independently represent the fusion sites with the oxazinic ring in the general formula (I) and the others, each independently, represent the hydrogen atom, a fluorine, chlorine or bromine atom, a methyl, isopropyl, trifluoromethyl, hydroxymethyl, benzyl, hydroxy, methoxy, amino, piperidino, morpholino, carboxyl, carboxymethyl, N,N-dimethylcarboxyamide, cyano, nitro, phenyl, acetyl or benzoyl group;
- two contiguous sustituents from R^8 to R^{13}, R^{14} to R^{21}, R^{22} to R^{28}, R^{30} to R^{35}, R^{36} to R^{41} represent the fusion sites with a benzene or quinone ring;
- at least one of the substituents from R-R^{41} represents what has already been described in point 7).

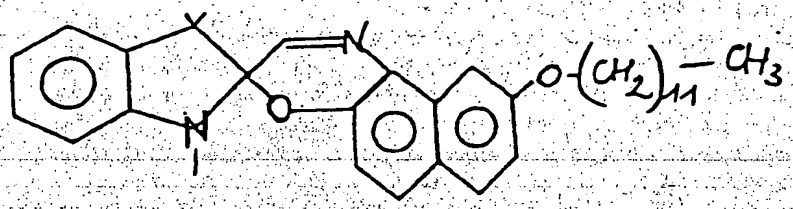
Specific examples of preferred photochromatic compounds according to the present invention, are:

- 1,3-dihydro-6'-N[2(octadecanoyloxy)ethyl]piperazino-1,3,3-trimethylspiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (Ia);



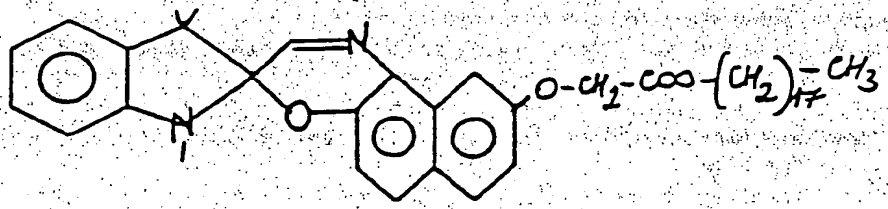
(Ia)

- 1,3-dihydro-9'-dodecyloxy-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (Ib);



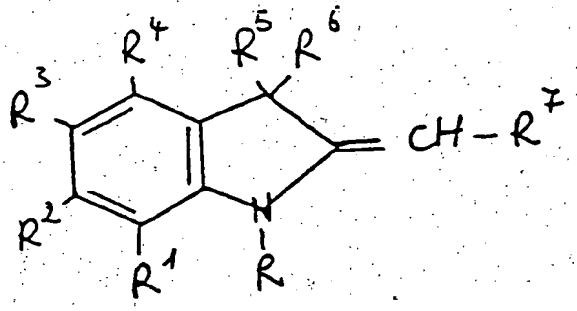
(Ib)

- 1,3-dihydro-9'-(octadecyloxyacetate)-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (Ic);



(Ic)

Compounds (I), of the present invention can be prepared by the reaction of a nitroso derivative of the compounds having formula (II), (III), (IV), (V), (VI), wherein two contiguous substituents from R^8 to R^{13}, from R^{14} to R^{21}, from R^{22} to R^{28}, from R^{30} to R^{35}, and from R^{35} to R^{41} represent one a -N=O group and the other a $-OR^{44}$ group, wherein R^{44} is a hydrogen atom; a metallic cation selected from sodium, potassium, lithium and copper cations; an ammonium or dialkyl (C_1-C_5) ammonium cation; a carbonylalkyl (C_1-C_5) group; an alkyl (C_1-C_5) sulphonyl group or an arylsulphonyl group; with a compound having formula (XIV):



(XIV)

wherein the substituents from R to R^7 have the above-defined meaning.

The nitroso derivatives of compounds (II), (III), (IV), (V), and (VI) can be prepared using the known methods described in Organic Synthesis Collective, vol. 3, page 411 or in U.S. Patent 3.285.972.

Compounds (XIV) can also be prepared with the known methods, as described in Journal American Chemical Society (1941), 63, page 2024 or in Bull. Soc. Chim. Frac. (1968), page 2066.

The reaction is generally carried out by adding compound (XIV) to a solution or suspension of the nitroso derivative of one of compounds (II), (III), (IV), (V) or (VI), in an inert organic solvent, possibly in the presence of a secondary or tertiary amine, operating at a temperature ranging from 0 to 150°C and preferably from 0 to 80°C, for periods of 1 minute to 24 hours.

The inert solvents which can be used for the reaction can be selected from aliphatic or aromatic hydrocarbons (such as pentane, hexane, heptane, benzene, toluene and xylene); chlorinated aliphatic or aromatic hydrocarbons (such as dichloromethane, 1,2-dichloroethane and chlorobenzene); aliphatic or aromatic ethers (such as diethyl ether, tetrahydrofuran and diphenylether); alcohols (such as methanol, ethanol, isopropanol and n-butanol); esters (such as ethyl acetate); amides (such as dimethylformamide); nitriles (such as acetonitrile); carbonates (such as dimethylcarbonate); and water.

In the reaction, the nitroso derivatives of compounds (II), (III), (IV), (V) or (VI) can be used in quantities ranging from 0.1 to 10 moles for each mole of compound (XIV), but preferably with equimolecular quantities.

When the reaction is carried out in the presence of a tertiary amine, this can be used in quantities of 0.1 to 2 moles for each mole of nitroso derivative, but preferably equimolecular quantities are used.

Examples of tertiary amines suitable for the purpose are: triethylamine, pyridine, 4-N,N-dimethylaminopyridine, N-methylpiperidine and N-methylmorpholine.

When the reaction is carried out in the presence of a secondary amine, this can be used in quantities ranging from 1 to 10 moles for each mole of nitroso derivative, but preferably from 2 to 5 moles.

Examples of secondary amines suitable for the purpose are: N-2-hydroxyethylpiperazine, N-2-aminoethylpiperazine and those described in EP Patent 245.020 and in IT Patent Application 22528 A/87 in the name of the same Applicant.

Alternatively, compounds (I) of the present invention can be prepared by the condensation of compounds having formula A, with a structure defined by the general formula (I), wherein the substituents and the nucleus P represent what has been previously described except for point 7) and at least one of the substituents from $R\text{-}R^{41}$ represents a hydroxy group, an amino group, a monoalkylamino group, an SH group directly linked to the spiro-oxazinic nucleus, by means of groups having formula $-O-(CH_2)_n-$, wherein n is an integer from 0 to 10, or by means of groups having formula (VII)-(XIII); with compounds having formula $R^{45}\text{-}CO\text{-}R^{46}$, wherein R^{45} represents a linear or branched $C_6\text{-}C_{30}$ alkyl group, a $C_6\text{-}C_{30}$ alkyl group substituted with 1-30 halogen atoms selected from fluorine, chlorine, bromine or iodine or a linear or branched $C_6\text{-}C_{30}$ alkenyl group and R^{46} represents a linear or branched $C_1\text{-}C_6$ alkoxy group, a hydroxy group, a halogen atom selected from chlorine, bromine or an imidazolic group.

The condensation is carried out under the conditions described in literature for the preparation of derivatives of carboxylic acids.

Compounds (I) of the present invention can also be prepared by the reaction between compounds having formula A, wherein the substituents and the nucleus P represent what is described above, and compounds having formula $R^{45}\text{-}X$, wherein R^{45} represents what has already been described and X is a halogen atom selected from chlorine, bromine or iodine, an acetate group, a methanesulphonate group or a p-toluene-sulphonate group.

In this case the reaction is generally carried out by mixing the reagents in a solvent or mixture of inert

solvents, possibly in the presence of basic compounds and/or phase transfer catalysts, operating at a temperature ranging from 0 to 200 °C, preferably from 10 to 120 °C, for periods of 1 minute to 48 hours.

Inert solvents which can be used for the reaction can be selected from aliphatic or aromatic hydrocarbons (such as pentane, hexane, heptane, benzene, toluene and xylene); chlorinated aliphatic or aromatic hydrocarbons (such as dichloromethane, 1,2-dichloroethane and chlorobenzene); aliphatic or aromatic ethers (such as diethyl ether, tetrahydrofuran and diphenylether); alcohols (such as methanol, ethanol, isopropanol and n-butanol); amides (such as dimethylformamide); ketones (such as acetone); nitriles (such as acetonitrile); dimethylsulphoxide; water; mixtures of at least one of the above organic solvents.

Compounds having formula A, intermediate products for the preparation of compounds (I), are prepared according to the procedure described in Patent Application IT 22528 A/87 in the name of the Applicant.

Compounds having formula R^{45}-X can be used in quantities ranging from 1 to 10 moles for each mole of the compound having formula A but preferably from 1 to 5 moles.

When the reaction is carried out in the presence of basic compounds, these can be used in quantities of 0.1 to 10 moles with respect to the compound having formula R^{45}-X but preferably from 1 to 5 moles.

Examples of basic compounds suitable for the purpose are: carbonates and bicarbonates of alkaline or earth-alkaline metals, such as sodium carbonate, potassium carbonate and calcium carbonate; tertiary amines such as triethylamine, pyridine, 4-N,N-dimethylaminopyridine, N-methylpiperidine and N-methylmorpholine; hydroxides of alkaline or earth-alkaline metals, such as sodium hydroxide, potassium hydroxide and calcium hydroxide; and mixtures of said compounds.

When the reaction is carried out under conditions of phase-transfer catalysis, the known methods may be used such as those described in "La Chimica e l'Industria", vol. 69 n.9, pages 94-98 (1987) and in the references cited therein.

A further method for the synthesis of compounds having formula (I) involves a condensation reaction between compounds having formula B, with a structure defined by general formula (I), wherein the substituents and the nucleus P represent what has been previously described except for point 7) and at least one of the substituents from R-R^{41} represents a CO-R^{47} group directly linked to the spiro-oxazinic nucleus, through groups having formula -O-$(CH_2)_n$-, wherein n is an integer from 0 to 10, or through groups having formula (VII)-(XIII); R^{47} represents a hydroxy group, a linear or branched C_1-C_6 alkoxy group, an imidazolic group, a halogen atom selected from chlorine or bromine; and compounds having the formula R^{48}-NH_2, R^{48}-R^{49}-NH, R^{48}-OH, R^{48}-SH wherein R^{48} and R^{49} represent a linear or branched C_6-C_{30} alkyl group, a C_6-C_{30} alkyl group substituted with 1-30 halogen atoms selected from fluorine, chlorine, bromine or iodine; a linear or branched C_6-C_{30} alkenyl group.

The condensation is carried out under the conditions described in literature for the preparation of derivatives of carboxylic acids.

In general, the products (I), synthesized according to one of the methods mentioned, are isolated using the normal techniques, such as for example, evaporation of the solvent under vacuum with subsequent purification of the raw product obtained by crystallization or chromatography.

Solvents suitable for crystallization include pentane, hexane, heptane, toluene, ethyl ether, methanol, ethanol, isopropanol, n-butanol, tetrahydrofuran, acetone, methylethylketone, ethyl acetate, dimethylcarbonate, acetonitrile and the relative mixtures of one or more of these.

Compounds (I) of the present invention are colourless or yellow, orange or red-coloured crystalline products.

Their solutions in common organic solvents, when not exposed to light sources, are colourless or slightly yellow or yellow-orange coloured.

When these solutions are exposed to a source of light (both visible and ultraviolet) they rapidly acquire a dark yellow, yellow-orange, red, blue or green colouring.

The colouring rapidly diminishes when the light source is removed.

The compounds having formula (I) can be applied either superficially or incorporated in the required articles, using the known techniques hereinafter described.

Some polymeric photochromatic products can be obtained with moulding techniques (for example injection or compression moulding) starting from suitable polymers in which the photochromatic compound is homogeneously dispersed in the mass.

Alternatively the photochromatic compound can be dissolved in a suitable solvent, together with the polymeric material (such as polymethyl methacrylate, polyvinyl alcohol, polyvinyl butyral, cellulose or epoxy, polysiloxanic or urethanic resin acetate butyrate) and deposited on a transparent support to form, after evaporation of the solvent, a photochromatic coating.

The photochromatic compound can also be added to a polymerizable monomer, for example methyl

methacrylate, so that, after polymerization carried out in the presence of a suitable initiator, such as azobisisobutyronitrile, they are uniformly incorporated in the resin formed.

According to another procedure, the photochromatic compound can be dissolved in a suitable solvent, in the presence of a resin, as described above, and a photochromatic film or plate containing the photochromatic compound uniformly dispersed can be formed from this solution, by evaporating the solvent.

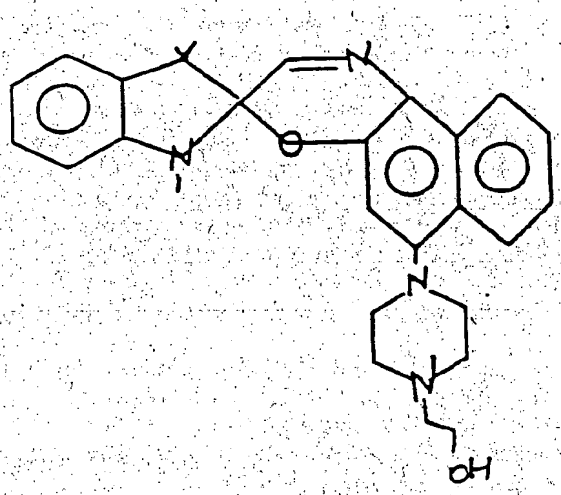
Finally the photochromatic compound can be applied to a transparent substrate (for example polycarbonate, polymethyl methacrylate or polydiethylene glycol bis(allyl carbonate)), by surface impregnation obtained by putting the substrate in contact with a solution or dispersion containing the photochromatic compound, at a suitable temperature.

Compounds (I) of the present invention have the characteristic of being able to be successfully incorporated, in mass or using one of the above techniques, also in polymers such as high density polyethylene, low density polyethylene, ethylene-vinylacetate copolymer or polyether amides whereas the compounds of the known art, in these substrates, tend to appear on the surface of the product making it consequently unusable.

The experimental examples which follow illustrate the present invention but do not limit it in any way.

EXAMPLE 1

Preparation of 1,3-dihydro-6'-N(-2-hydroxyethyl) piperazino-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine (A1).



(A1)

20 g (153.8 mmoles) of N-2-hydroxyethyl piperazine and 5 g (28.9 mmoles) of 1,3,3,-trimethyl-2-methylene indoline are added, under a nitrogen flow, to a suspension of α-nitrose β-naphthol (10 g, 57.8 mmoles) in toluene (150 ml).

The resulting mixture is heated for 4 hours and 30 minutes before removing the solvent with a rotating evaporator.

120 ml of methanol are added to the residue and, after heating to reflux temperature, the resulting mixture is kept for 12 hours at room temperature.

The solid which has formed is filtered away and the limpid solution is dried at reduced pressure.

The residue obtained is dissolved in 120 ml of methylene chloride and the resulting solution is washed with 350 ml of water.

The solvent is removed from the organic phase, anhydrified on sodium sulphate, by means of the rotating evaporator.

The residue is dissolved under heat in 20 ml of methanol and the resulting solution is kept for 2 hours at room temperature.

A precipitate is formed which is filtered on buchener and washed with fresh methanol.

3.5 g of a greyish-white product are obtained which is used without further purification.

It was characterized as follows:

- m.p. (measured in Differential Scanning Calorimetry or DSC): 168.2° C.
- Mass spectrometry (m/e): ion $[MH]^+$: 456
- ^{1}H-NMR (200 MHz, $CDCl_3$-TMS) δ (ppm): 1.33 (6H,s, 2 CH_3 in 3); 2.5-2.9 (10H, m, NCH_3, OH and 6H aliphatic); 3.0-3.15 (4H, m, H aliphatic); 3.65 (2H, t, -CH_2OH); 6.55 (1H, d, H in 7); 6.58 (1H, s, H in 5'); 6.87 (1H, t, H in 5); 7.07 (1H, d, H in 4); 7.19 (1H, t, H in 6); 7.34 (1H, t, H in 8'); 7.53 (1H, t, H in 9'); 7.61 (1H, s, CH on N); 8.0 (1H, d, H in 7'); 8.52 (1H, d, H in 10').

EXAMPLE 2

Preparation of 1,3-dihydro-6'-N[2(octadecanoyloxy)ethyl] piperazino-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (Ia).

1 ml of triethylamine and 0.81 ml (0.73 g = 2.4 mmoles) of stearoyl chloride are added to a solution of 1,3-dihydro-6'-N(-2-hydroxyethyl) piperazino-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth- (2,1b)-(1,4) oxazine] (Al) (1g, 2,2 mmoles) in toluene (20 ml).

3 ml of triethylamine and 1.4 ml of acyl chloride are added to the reaction mixture over a period of 8 hours.

After an hour at room temperature, the resulting mixture is treated with 60 ml of 3.5% NaOH.

An emulsion is formed which is extracted 4 times with 100 ml of methylene chloride.

The reddish-purple coloured organic extracts are put together and anhydrified on sodium sulphate.

After the anhydrifying agent has been eliminated by filtration, 5 g of silica are added to the limpid solution.

The solvent is removed from the resulting suspension by the rotating evaporator, and a blue powder is obtained which is charged into a glass column containing 3 g of clean silica.

The silica column is eluated with 120 ml of ethyl acetate, and a reddish-purple solution is obtained from which the solvent is removed by means of the rotating evaporator.

Upon recrystallization of the residue with hexane (15 ml), 1.1 g of a white product is obtained.

It has been characterized as follows:

- Mass spectrometry (m/e): ion $[MH]^+$: 722.
- ^{1}H-NMR (200 MHz, $CDCl_3$-TMS) δ (ppm): 0.85 (3H, t, CH_3 of the aliphatic chain); 1.14-1.4 (34H, m, aliphatic chain plus 2 methyl groups in 3); 1.5-1.7(2H, m, -CH_2-CH_2-COO-); 2.3 (2H, t, -CH_2-COO-); 2.67-2.86 (9H, m, NCH_3 and 6H aliphatic); 3.0-3.2 (4H, m, -$(CH_2)_2$N); 4.24 (2H, t, CH_2OCO); 6.55 (1H, d, H in 7); 6.57 (1H, s, H in 5'); 6.87 (1H, t, H in 5); 7.07 (1H, d, H in 4); 7.19 (1H, t, H in 6); 7.34 (1H, t, H in 8'); 7.52 (1H, t, H in 9'); 7.61 (1H, s, CH on N); 7.99 (1H, d, H in 7'); 8.52 (1H, d, H in 10').

EXAMPLE 3

Preparation of 1,3-dihydro-9'-dodecyloxy-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (Ib).

2 ml of triethylamine, 1 ml (4.16 mmoles) of 1-bromo dodecane and 0.2 g of Na_2CO_3 are added in this order to a suspension of 1,3-dihydro-9'-hydroxy-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (prepared according to JP 90/41,388) (350 mg, 1 mmole) in toluene (5 ml).

The resulting mixture is heated to reflux temperature for 8 hours and, after one night at room temperature, 10 ml of water and 10 ml of toluene are added.

When the phases have been separated, the organic phase is washed with a further 10 ml of water and then anhydrified on sodium sulphate.

On eliminating the solvent at reduced pressure, a residue is obtained which is crystallized with hexane (10 ml).

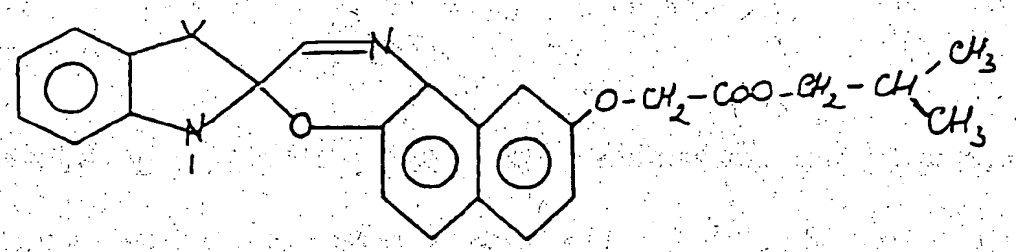
230 mg of a white product are obtained.

It was characterized as follows:

- Mass spectrometry (m/e): ion $[MH]^+$: 512.
- ^{1}H-NMR (200 MHz, $CDCl_3$-TMS) δ (ppm): 0.86 (3H, t, CH_3 of the aliphatic chain); 1-2 (26H, m, H aliphatic); 2.73 (3H, s, NCH_3); 4.15 (2H, t, -CH_2O); 6.55 (1H, d, H in 7); 6.81 (1H, d, H in 5'); 6.87 (1H, t, H in 5); 7.01 (1H, dd with J metha, H in 8'); 7.06 (1H, d, H in 4); 7.19 (1H, dt with J metha, H in 6); 7.54 (1H, d, H in 6'); 7.59 (1H, d, H in 7'); 7.69 (1H, s, CH on N); 7.81 (1H, d with J metha, H in 10').

EXAMPLE 4

Preparation of 1,3-dihydro-9'(isobutyloxyacetate)-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (B1).



(B1)

3 g (55 mmoles) of sodium methylate are added to a suspension of 1,3-dihydro-9'-hydroxy-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (prepared according to JP 90/41,388) (17 g, 50 mmoles) in isobutylic alcohol (60 ml), kept under a nitrogen flow at 80 °C. 9.2 g (55 mmoles) of ethyl bromo acetate are added to the dark solution obtained.

The mixture is then heated to 80 °C for 1 hour before adding 30 ml of toluene necessary for dissolving the precipitate which has formed.

After a further hour at 80 °C, the reaction mixture is cooled to room temperature before adding 50 ml of water and 3 g of active carbon.

The resulting suspension is filtered and the organic phase is separated from the aqueous solution.

The solvent is removed from the organic solution obtained with the rotating evaporator and the residue crystallized by adding 50 ml of ethyl alcohol.

16 g of a yellow product are thus obtained.

It was characterized as follows:

- Mass spectrometry (m/e): ion $[MH]^+$: 458.
- ^{1}H-NMR (200 MHz, $CDCl_3$-TMS) δ (ppm): 0.92 (6H, d, the CH_3 of the isobutyl group); 1.32 (3H,s a CH_3 in 3); 1.33 (3H, s, a CH_3 in 3); 2.0 (1H, m, CH of the isobutyl group); 2.73 (3H, s, NCH_3); 4.03 (2H, d, $-CH_2-$ of the isobutyl group); 4.83 (2H, s, $-O-CH_2-COO-$); 6.55 (1H, d, H in 7); 6.83 (1H, d, H in 5'); 6.87 (1H, t, H in 5); 7.04-7.23 (3H, m, H in 4, H in 6 and H in 8'); 7.55 (1H, d, H in 6'); 7.64 (1H, d, H in 7'); 7.67 (1H, s, CH on N); 7.8 (1H, d with J metha, H in 10').

EXAMPLE 5

Preparation of 1,3-dihydro-9'-(octadecyloxyacetate)-1,3,3-trimethyl spiro [2H indole-2,3'-[3H] naphth-(2,1b)-(1,4) oxazine] (Ic).

0.33 g (1.2 mmoles) of stearylic alcohol and 25 mg of tin dibutyl dilaurate are added to a solution of 1,3-dihydro-9'-(isobutyloxyacetate)-1,3,3-trimethyl spiro [2H indole-2,3'-[3H] naphth-(2,1b)-(1,4) oxazine] (B1) (0.5 g, 1.1 mmoles) in toluene (10 ml).

The resulting solution is heated to reflux temperature for 15 hours continuously distilling the solvent and replacing it with fresh toluene.

The solvent is then removed from the resulting mixture in the rotating evaporator and the residue is recrystallized with isopropylic alcohol.

The solid is filtered on büchener and then washed with isopropanol and methanol.

0.6 g of a white solid are thus obtained.

It was characterized as follows:

- m.p. (measured in Differential Scanning Calorimetry or DSC): 72.7 °C.
- Mass spectrometry (m/e): ion $[MH]^+$: 654.
- ^{1}H-NMR (200 MHz, $CDCl_3$-TMS) δ (ppm): 0.85 (3H, t, CH_3 of the aliphatic chain); 1.1-1.4 (36H, m, 6H of the two methyls in 3 and 30H of the $-CH_2-$ of the aliphatic chain); 1.68 (2H, t, $-CH_2-CH_2-O-$); 2.73 (3H, s, NCH_3); 4.22 (2H, t, $-CH_2OCO$); 4.81 (2H, s, $-O-CH_2-COO$); 6.55 (1H, d, H in 7); 6.84 (1H, d, H in 5'); 6.87 (1H, t, H in 5); 7.07 (1H, d, H in 4); 7.13 (1H, dd with J metha, H in 8'); 7.55 (1H, d, H in 6'); 7.64 (1H, d, H in 7'); 7.68 (1H, s, CH on N); 7.8 (1H, d, with J metha, H in 10').

EXAMPLE 6

Four mixtures are prepared (n. 1-4 in Table 1) composed of low density polyethylene in granules (Riblene CF 2200U - Enichem), of the stabilizer UV Chimasorb 944U (Ciba Geigy) and, in cases 2, 3 and 4 respectively, of photochromatic compounds AI, Ia and the compound 1,3-dihydro-6'-piperidino-1,3,3-trimethylspiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] in the weight ratios specified in Table 1.

TABLE 1

Mixture number	UV stabilizer (% w/w)	Photochromatic compound (% w/w)
1	0.2	---
2	0.2	0.11
3	0.2	0.175
4	0.2	0.1

The photochromatic compounds were used in different weight quantities to obtain equal molar concentrations.

The mixtures obtained were transformed into films with a thickness of 150 μm by means of extrusion.

The extrusions were carried out in a Plasticorder Brabender equipped with a 19 mm diameter barrel.

The temperature profile along the extruder was: 170 °C - 180 °C - 190 °C - 200 °C - 210 °C.

The photochromatic films obtained were evaluated by visual inspection, immediately after preparation and then replaced in darkness.

The evaluations were repeated after 7 and after 60 days. The results are shown in Table 2.

TABLE 2

Mixture number	Evaluation immediately after film preparation	Evaluation after seven days	Evaluation after sixty days
1	Transparent, homogeneous film	Transparent, homogeneous film	Transparent, homogeneous film
2	"	"	Very evident blooming
3	"	"	Transparent, homogeneous film
4	"	Traces of blooming	Very evident blooming

Blooming has a negative effect on the photochromatic activity of the product, as can be seen in Table 3 which shows the optical density values (D.O.) of the film at 358 nanometres (nm) (I_{max} of the colourless form) and the transmittance percentage variation at 25 °C (DT) between 400 and 700 nanometres associated with the activation process.

TABLE 3

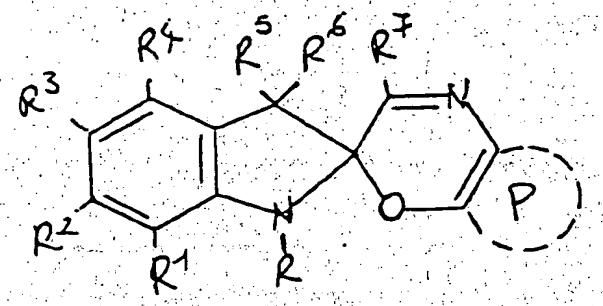
Mixture number	D.O. (358 nm)	DT (25 °C)
2	0.458	0.57
3	0.573	18.52
4	0.468	6.79

The films were activated by irradiation for 30 seconds with a UVA lamp with an irradiation of 9 W/m^2.

The D.O. and DT measurements were carried out with a HP 8452A spectrophotometer with a photodiode array detector.

Claims

1. Photochromatic and thermochromatic compounds, belonging to the group of spiro-indoline-oxazines, which can be defined with the following general formula (I):



(I)

wherein:

1) R represents a hydrogen atom; a linear or branched C_1-C_5 alkyl group; a C_1-C_5 alkyl group substituted with from 1 to 5 halogen atoms selected from fluorine, chlorine, bromine and iodine, hydroxy groups, C_1-C_5 alkoxy groups, C_1-C_5 alkyl carboxy groups, cyano groups; a C_2-C_5 alkenyl group; a phenyl group; a benzyl group;

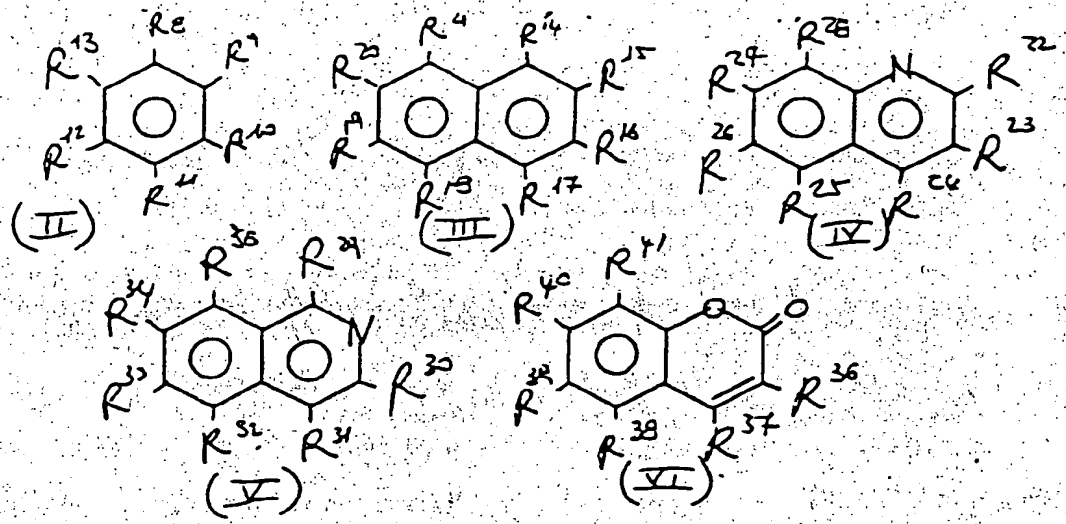
2) R^1 to R^4, the same or different, each independently represent a hydrogen atom; a linear or branched C_1-C_5 alkyl group; a C_1-C_5 alkyl group substituted with 1 to 5 halogen atoms selected from fluorine, chlorine, bromine and iodine, hydroxy groups, C_1-C_5 alkoxy groups, C_1-C_5 alkyl carboxy groups, cyano groups; a C_2-C_5 alkenyl group; a benzyl group; a halogen atom selected from fluorine, chlorine, bromine and iodine; a hydroxy group; a C_1-C_5 alkoxy group; an amino group; a mono-alkyl (C_1-C_5 amino group, a di-alkyl (C_1-C_5) amino group; a cyclo-alkyl (C_3-C_{10}) amino group; a piperidino, piperazino or morpholino group; a carboxyl group; a C_1-C_5 alkyl carboxy group; a C_2-C_5 alkenyl carboxy group; an amidic carboxy group; a substituted N-alkyl (C_1-C_5) amidic carboxy group; a substituted N,N-dialkyl (C_1-C_5) amidic carboxy group; a cyano group; a nitro group; a sulphonic group; a sulphonic alkyl (C_1-C_5) group; a trifluoromethan-sulphonic group; a sulphonic aryl group selected from benzene sulphonic, p-toluene sulphonic, p-chlorotoluene sulphonic groups; an aryl group selected from phenyl, biphenyl, naphthyl groups; an acylic group of the alkyl ketonic, aryl ketonic or benzyl ketonic type;

3) two consecutive substituents from R^1 to R^4 can represent the fusion points with other aromatic, heterocyclic or quinonic rings;

4) R^5 and R^6, the same or different, each independently represent a linear or branched C_1-C_5 akyl group; a phenyl group; or R^5 and R^6, together with the carbon atom to which they are linked, jointly represent a C_4-C_7 cycloalkyl group;

5) R^7 represents a hydrogen atom; a linear or branched C_1-C_5 alkyl group; a phenyl group; a halogen atom selected from fluorine, chlorine and bromine; a C_1-C_5 alkoxy group, a phenoxy group;

6) P represents a monocyclic or polycyclic arenic nucleus, of the benzene, naphthalene, quinoline, isoquinoline or cumarine type which can be respectively represented with the formulae (II), (III), (IV), (V) and (VI):



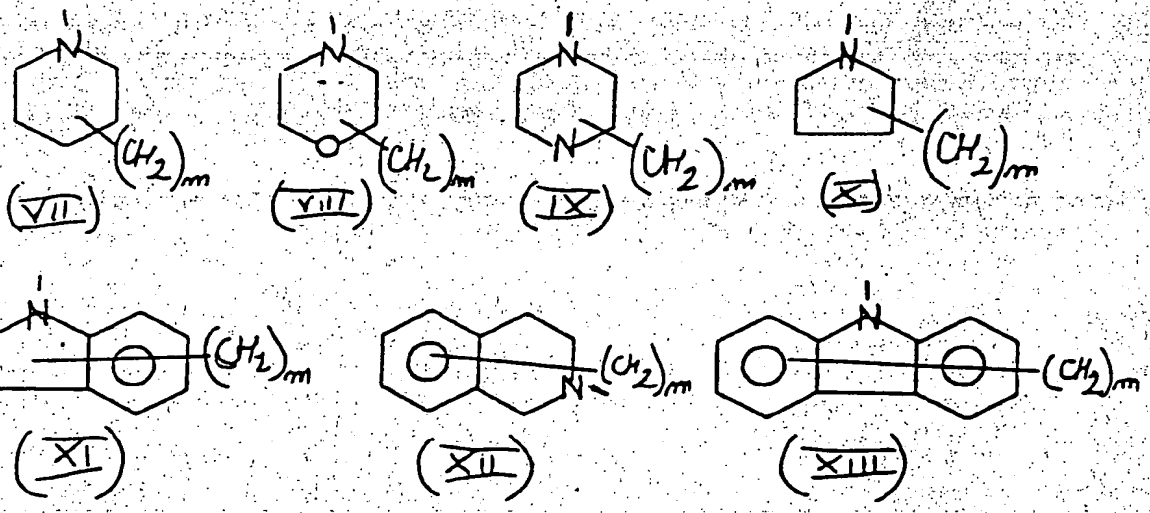
wherein:

6a) at least two contiguous substituents from R^8 to R^{13}, R^{14} to R^{21}, R^{22} to R^{28}, R^{30} to R^{35}, R^{36} to R^{41} represent the fusion sites with the oxazinic ring;

6b) the substituents from R^8 to R^{41} have the meaning defined in point 2);

7) at least two of the substituents selected from R-R^{41} represents an R^{42} group, a $-COOR^{42}$, $-CONHR^{42}$, $-CONR^{42}R^{43}$, $-COR^{42}$, OH-CH-R^{42}, OH-C-$R^{42}R^{43}$, $-OR^{42}$, $-NHR^{42}$, $-NR^{42}R^{43}$, $-SR^{42}$, $-O-(CH_2)_n-COOR^{42}$, $-O-(CH_2)_n-CONHR^{42}$, $-O-(CH_2)-CONR^{42}R^{43}$ group, wherein n varies from 0 to 10 and R^{42} and R^{43} can be independently a linear or branched C_6-C_{30} alkyl group; a C_6-C_{30} alkyl group substituted with 1-30 halogen atoms selected from fluorine, chlorine, bromine or iodine; a C_6-C_{30} alkenyl group;

8) the substituents R^1-R^{41} can otherwise be groups



wherein m is an integer from 0 to 10.

2. Photochromatic and thermochromatic compounds belonging to the group of spiro-indoline-oxazines, according to Claim 1, whose preferred forms, referring to general formula (I), are those wherein:
   - R represents a methyl, ethyl, benzyl, 2-allyl, 2-hydroxyethyl, 2-methoxyethyl or 2-carboxymethylethyl group;
   - R^1 to R^4, the same or different, each independently represent the hydrogen atom, a fluorine,

chlorine or bromine atom, a methyl, isopropyl, trifluoromethyl, hydroxymethyl, benzyl, hydroxy, methoxy, amino, piperidino, morpholino, carboxyl, carboxymethyl, N,N-dimethylcarboxyamide, cyano, nitro or phenyl group;
- R^5 and R^6, the same or different, each independently represent a methyl or phenyl group, or, together with the carbon atom to which they are linked, jointly represent the cyclohexyl group;
- R^7 represents the hydrogen atom, chlorine atom or phenyl, methyl or methoxy group;
- P is one of the groups with formula from (II) to (VI) wherein:
- two contiguous substituents from R^8 to R^{13}, R^{14} to R^{21}, R^{22} to R^{28}, R^{30} to R^{35}, R^{36} to R^{41} independently represent the fusion sites with the oxazinic ring in general formula (I) and the others each independently represent the hydrogen atom, a fluorine, chlorine or bromine atom, a methyl, isopropyl, trifluoromethyl, hydroxymethyl, benzyl, hydroxy, methoxy, amino, piperidino, morpholino, carboxyl, carboxymethyl, N,N-dimethylcarboxyamide, cyano, nitro, phenyl, acetyl or benzoyl group;
- two contiguous substituents from R^8 to R^{13}, R^{14} to R^{21}, R^{22} to R^{28}, R^{30} to R^{35}, R^{36} to R^{41} represent the fusion sites with a benzenic or quinonic ring;
- at least one of the substituents from R-R^{41} represent what has already been described in point 7).

3. Photochromatic and thermochromatic compound belonging to the group of spiro-indoline-oxazines, according to Claim 2, having the formula:
   - 1,3-dihydro-6'-N[2(octadecanoyloxy)ethyl] piperazino-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphtho-(2,1b)-(1,4) oxazine] (Ia).

4. Photochromatic and thermochromatic compound belonging to the group of spiro-indoline-oxazines, according to Claim 2, having the formula:
   - 1,3-dihydro-9'-dodecyloxy-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (Ib).

5. Photochromatic and thermochromatic compound belonging to the group of spiro-indoline-oxazines, according to Claim 2, having the formula:
   - 1,3-dihydro-9'-(octadecyloxyacetate)-1,3,3-trimethyl spiro [2H indole-2,3'-[3H]-naphth-(2,1b)-(1,4) oxazine] (Ic).

6. Photochromatic polymeric composition composed of at least one compound having general formula (I) and at least one polymer selected from high density polyethylene, low density polyethylene, ethylene-vinylacetate copolymer, polyether amides, polymethyl methacrylate, polyvinyl alcohol, polyvinyl butyral, cellulose acetate butyrate, epoxy, polysiloxane or urethane resins, polycarbonate, polydiethylene glycol bis(allyl carbonate).

7. Photochromatic polymeric composition, according to Claim 6, composed of at least one compound having general formula (I) and low density polyethylene.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2186

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 230 024 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) * claims; examples 1,3 *	1,2,5	G03C1/685 C07D498/10
X,P	EP-A-0 449 669 (TOKOYAMA SODA KABUSHIKI KAISHA) * claims; examples 12,8 *	1,2	
X	EP-A-0 277 639 (TORAY INDUSTRIES, INC.) * claims *	1,2	
X	EP-A-0 146 135 (OPTISCHE WERKE G. RODENSTOCK) * claims *	1,2	
X	EP-A-0 350 009 (KUREHA KAGAKU KOGYO K.K.) * example 10 *	1,2	
X	WORLD PATENTS INDEX LATEST Section Ch, Week 9130, Derwent Publications Ltd., London, GB; Class A, AN 91-217705 & JP-A-3 137 634 (DAINIPPON INK CHEM INK KK) 12 June 1991 * abstract *	1,2	
X	WORLD PATENTS INDEX LATEST Section Ch, Week 9125, Derwent Publications Ltd., London, GB; Class E, AN 91180613 & JP-A-3 107 839 (HITACHI KK) 8 May 1991 * abstract *	1,2	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C
C07D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 SEPTEMBER 1992	HILLEBRECHT D.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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